

Dioxygen-Initiated Oxidation of Heteroatomic Substrates Incorporated into Ancillary Pyridine Ligands of Carboxylate-Rich Diiron(II) Complexes

Emily C. Carson and Stephen J. Lippard*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Progress toward the development of functional models of the carboxylate-bridged diiron active site in soluble methane monooxygenase is described in which potential substrates are introduced as substituents on bound pyridine ligands. Pyridine ligands incorporating a thiol, sulfide, sulfoxide, or phosphine moiety were allowed to react with the preassembled diiron(II) complex $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^R)_2(\text{O}_2\text{CAR}^R)_2(\text{THF})_2]$, where O_2CAR^R is a sterically hindered 2,6-di(*p*-tolyl)- or 2,6-di(*p*-fluorophenyl)benzoate ($R = \text{Tol}$ or 4-FPh). The resulting diiron(II) complexes were characterized crystallographically. Triply and doubly bridged compounds $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tol}})_3(\text{O}_2\text{CAR}^{\text{Tol}})(2\text{-MeSpy})]$ (**4**) and $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tol}})_2(\text{O}_2\text{CAR}^{\text{Tol}})_2(2\text{-MeS(O)py})_2]$ (**5**) resulted when 2-methylthiopyridine (2-MeSpy) and 2-pyridylmethylsulfoxide (2-MeS(O)py), respectively, were employed. Another triply bridged diiron(II) complex, $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{4\text{-FPh}})_3(\text{O}_2\text{CAR}^{4\text{-FPh}})(2\text{-Ph}_2\text{Ppy})]$ (**3**), was obtained containing 2-diphenylphosphinopyridine (2-Ph₂Ppy). The use of 2-mercaptopyridine (2-HSpy) produced the mononuclear complex $[\text{Fe}(\text{O}_2\text{CAR}^{\text{Tol}})_2(2\text{-HSpy})_2]$ (**6a**). Together with that of previously reported $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tol}})_3(\text{O}_2\text{CAR}^{\text{Tol}})(2\text{-PhSpy})]$ (**2**) and $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tol}})_3(\text{O}_2\text{CAR}^{\text{Tol}})(2\text{-Ph}_2\text{Ppy})]$ (**1**), the dioxygen reactivity of these iron(II) complexes was investigated. A dioxygen-dependent intermediate (**6b**) formed upon exposure of **6a** to O₂, the electronic structure of which was probed by various spectroscopic methods. Exposure of **4** and **5** to dioxygen revealed both sulfide and sulfoxide oxidation. Oxidation of **3** in CH₂Cl₂ yields $[\text{Fe}_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CAR}^{4\text{-FPh}})(\text{O}_2\text{CAR}^{4\text{-FPh}})_3(\text{OH}_2)(2\text{-Ph}_2\text{P(O)py})]$ (**8**), which contains the biologically relevant $\{\text{Fe}_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CR})\}_3^{3+}$ core. This reaction is sensitive to the choice of carboxylate ligands, however, since the *p*-tolyl analogue **1** yielded a hexanuclear species, **7**, upon oxidation.

Introduction

Dioxygen activation and O-atom transfer reactions promoted by iron-containing metalloenzymes are of considerable interest both for ecological and industrial applications.^{1,2} Soluble methane monooxygenase (sMMO) is one such enzyme system that is used by methanotropic bacteria to catalyze the selective conversion of methane to methanol.³ In addition to saturated hydrocarbons, olefins, methanethiol, amines, and sulfides can act as substrates.^{3–6} A carboxylate-bridged non-heme diiron active site, housed in the hydroxy-

lase component (MMOH) of sMMO, is responsible for the binding and reductive activation of dioxygen.^{7–10} In the reduced state (MMOH_{red}), the diiron(II) centers are bridged by two carboxylates and each has an additional monodentate carboxylate ligand. One of the latter is involved in hydrogen bonding with a coordinated water molecule. In the oxidized, resting state of the enzyme (MMOH_{ox}), the diiron(III) center is bridged by two hydroxide ions and a single carboxylate group. The other three carboxylate residues are monodentate, one of which is hydrogen bonded to a coordinated water molecule. Representations of MMOH_{red} and MMOH_{ox} are provided in Chart 1.

* To whom correspondence should be addressed. E-mail: lippard@mit.edu.

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Chart 1

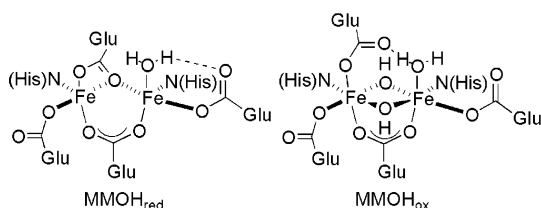
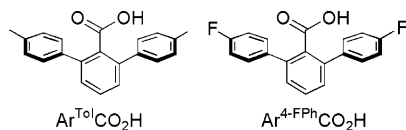


Chart 2



The preparation and study of structural, spectroscopic, and functional models for the active sites in metalloproteins have provided insight into the mechanisms of their oxidation chemistry, enhancing and extending our understanding of the natural systems.¹¹ A variety of symmetric diiron complexes carrying N-donor and assorted O-donor ligands have been reported as mimics for the diiron sites in MMOH and related enzymes.^{12–14} Complexes with two carboxylate ligands per iron atom are necessary to provide an accurate representation of the MMOH active site. Self-assembly of discrete dinuclear centers with such carboxylate ligands is challenged by their tendency to form oligomers.^{15–20} Terphenyl-based carboxylate ligands facilitate the assembly of discrete dinuclear complexes and mimic to some degree the hydrophobic pocket present at the protein active sites (Chart 2).^{21–23}

In addition to four carboxylate ligands, two nitrogen donors are required to replicate the stoichiometry of the diiron core at the MMOH active site. One approach to emulate enzyme functionally is to tether a substrate to the N-donor ligand, increasing its chances of reacting with a dioxygen-activated dimetallic core. The introduction of dioxygen into solutions of the diiron(II) complexes $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tol}})_2(\text{O}_2\text{CAR}^{\text{Tol}})_2(N,N\text{-Bn}_2\text{en})_2]$,^{24,25} where $\text{O}_2\text{CAR}^{\text{Tol}}$ is 2,6-di(*p*-tolyl)-benzoate and *N,N*-Bn₂en is *N,N*-dibenzylethylenediamine, $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tol}})_4(\text{BA}^{p\text{-OMe}})_2]$,²⁶ where $\text{BA}^{p\text{-OMe}}$ is *p*-methoxybenzylamine, and $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tol}})_4(\text{NH}_2(\text{CH}_2)_2\text{Sbn})_2]$,^{27a} led to the evolution of benzaldehyde. This chemistry is formally the result of intramolecular

benzylic hydroxylation followed by dealkylation. The strategy has been extended to include benzyl- or ethyl-derivatized pyridine ligands, which react to form the corresponding alcohol, ketone, or both.^{27b,28}

In addition to C–H activation, the carboxylate-rich diiron center in MMOH is capable of oxidizing alkyl sulfides and thiols.^{3,6} We therefore extended our studies to examine carboxylate-bridged diiron(II) complexes with pyridine ligands incorporating thiol, sulfide, sulfoxide, and phosphine as tethered substrates. Upon exposure to dioxygen, these complexes react to form the corresponding sulfoxide, sulfone, and phosphine oxide. The results of this study, a portion of which has been previously communicated,²⁸ are reported here.

Experimental Section

General Considerations. All reagents were obtained from commercial suppliers and used as received, unless otherwise noted. Dichloromethane and pentane were saturated with nitrogen and purified by passage through activated Al_2O_3 columns under argon.²⁹ Dioxygen (99.994%, BOC Gases) was dried by passing the gas stream through a column of Drierite. The synthesis and characterization of $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tol}})_2(\text{O}_2\text{CAR}^{\text{Tol}})_2(\text{THF})_2]$, $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tol}})_3(\text{O}_2\text{CAR}^{\text{Tol}})(2\text{-Ph}_2\text{Ppy})]$ (**1**), and $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tol}})_3(\text{O}_2\text{CAR}^{\text{Tol}})(2\text{-PhSpy})]$ (**2**) were reported previously.^{21,28} 2-Phenylthiopyridine (2-PhSpy), 2-phenylpyridylsulfoxide (2-PhS(O)py), 2-methylthiopyridine (2-MeSpy), 2-methylpyridylsulfoxide (2-MeS(O)py), and 2-methylpyridylsulfone (2-MeS(O)₂py) were prepared by modified literature procedures, and their purity was confirmed by ¹H NMR spectroscopy.³⁰ 2-Pyridyldiphenylphosphine oxide (2-Ph₂P(O)py) was synthesized according to a published procedure,³¹ and the purity was checked by ¹H and ³¹P NMR spectroscopy. Air-sensitive manipulations were carried out under nitrogen in an Mbraun drybox. All samples were pulverized and dried under vacuum at 60 °C to remove solvent prior to determining their elemental composition.

$[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{4\text{-FPh}})_3(\text{O}_2\text{CAR}^{4\text{-FPh}})(2\text{-Ph}_2\text{Ppy})]$ (**3**). 2-Ph₂Ppy (28.5 mg, 0.108 mmol) was added to a CH_2Cl_2 (4 mL) solution of $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{4\text{-FPh}})_2(\text{O}_2\text{CAR}^{4\text{-FPh}})_2(\text{THF})_2]$ (150 mg, 0.100 mmol) to form an orange solution that was stirred for 20 min. Diffusion of pentane into the reaction mixture yielded orange block crystals (151 mg, 93%) of **3**. FT-IR (KBr, cm^{-1}): 3062 (w), 2954 (w), 2863 (w), 1891 (w), 1604 (s), 1560 (m), 1510 (s), 1455 (s), 1406 (s), 1380 (s), 1299 (w), 1221 (s), 1158 (s), 1093 (m), 1049 (w), 1015 (m), 841 (m), 833 (m), 806 (s), 791 (m), 767 (m), 747 (w), 701 (m), 582 (w), 554 (s), 528 (s), 502 (w), 463 (w), 417 (w). Anal. Calcd for $\text{C}_{93}\text{H}_{58}\text{NFe}_2\text{O}_8\text{F}_8\text{P}$: C, 69.29; H, 3.63; N, 0.87; P, 1.92. Found: C, 68.92; H, 3.70; N, 1.11; P, 1.68.

$[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tol}})_3(\text{O}_2\text{CAR}^{\text{Tol}})(2\text{-MeSpy})]$ (**4**). In a CH_2Cl_2 (4 mL) solution, $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tol}})_2(\text{O}_2\text{CAR}^{\text{Tol}})_2(\text{THF})_2]$ (114 mg, 0.782 mmol) was allowed to react with 2-MeSpy (21.6 mg, 0.173 mmol) for 15 min. Removal of the solvent under reduced pressure left a residue that was extracted into 2 mL of dichloroethane. Diffusion of pentane vapor into the bright orange-yellow solution yielded yellow block crystals (0.106 mg, 94%) of **4** suitable for X-ray crystallography. FT-IR (KBr, cm^{-1}): 3050 (w), 3023 (w), 2918

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(w), 2860 (w), 1601 (s), 1576 (m), 1559 (m), 1513 (s), 1453 (s), 1406 (s), 1382 (s), 1304 (w), 1283 (w), 1185 (w), 1149 (w), 1109 (w), 1071 (w), 1019 (m), 970 (w), 832 (w), 817 (s), 799 (s), 765 (s), 737 (m), 702 (s), 641 (m), 608 (w), 583 (m), 557 (w), 523 (m), 465 (m), 410 (w). Anal. Calcd for $C_{90}H_{75}NO_8SFe_2 \cdot 0.5C_2H_4Cl_2$: C, 73.27; H, 5.20; N, 0.94. Found: C, 73.29; H, 5.45; N, 1.12.

[Fe₂(μ-O₂CAr^{Tol})₂(O₂CAr^{Tol})₂(2-MeS(O)py)₂] (5). A bright red-orange solution was produced upon the addition of 2-MeS(O)py (28.2 mg, 0.200 mmol) to [Fe₂(μ-O₂CAr^{Tol})₂(O₂CAr^{Tol})₂(THF)₂] (98.9 mg, 0.0677 mmol) in 6 mL of CH₂Cl₂, and a red powder (91.8 mg, 85%) was isolated after diffusion of pentane into the reaction mixture. Red block crystals of **5** suitable for X-ray diffraction studies were obtained by diffusing pentane vapor into a chlorobenzene solution of **5**. FT-IR (KBr, cm⁻¹): 3053 (w), 3022 (w), 2917 (w), 2862 (w), 1588 (s), 1562 (s), 1540 (s), 1514 (s), 1454 (s), 1410 (s), 1376 (s), 1304 (w), 1263 (w), 1186 (w), 1147 (w), 1109 (w), 1088 (w), 1020 (m), 1008 (s), 967, 818 (s), 800 (s), 785 (s), 765 (s), 737 (m), 711 (m), 703 (m), 637 (m), 608 (w), 584 (m), 542 (w), 520 (m), 450 (w), 411 (w). Anal. Calcd for C₉₆H₈₂N₂-Fe₂O₁₀S₂: C, 72.09; H, 5.17; N, 1.75. Found: C, 71.71; H, 4.85; N, 1.81.

[Fe(O₂CAr^{Tol})₂(2-HSPy)₂] (6a). A solution of [Fe₂(μ-O₂CAr^{Tol})₂(O₂CAr^{Tol})₂(THF)₂] (174 mg, 0.119 mmol) in CH₂Cl₂ (4 mL) was combined with 2-mercaptopyridine (2-HSPy) (62.9 mg, 0.566 mmol) and stirred for 15 min. Vapor diffusion of pentane into this orange solution produced orange blocks of **6a** (199 mg, 95%) suitable for X-ray crystallography. FT-IR (KBr, cm⁻¹): 3195 (w), 3114 (w), 3053 (w), 2916 (w), 2862 (w), 1591 (s), 1539 (s), 1514 (s), 1446 (s), 1410 (s), 1375 (s), 1269 (w), 1130 (s), 1085 (w), 1020 (w), 995 (m), 916 (w), 847 (w), 818 (m), 801 (s), 786 (m), 755 (s), 726 (m), 707 (m), 619 (w), 584 (w), 539 (w), 521 (m), 486 (w), 442 (m). Anal. Calcd for C₅₂H₄₄N₂FeO₄S₂: C, 70.90; H, 5.03; N, 3.18. Found: C, 71.81; H, 4.91; N, 3.32.

[Fe₆(μ₄-O)₂(μ-OH)₆(μ-O₂CAr^{Tol})₄Cl₄(2-Ph₂P(O)py)₂] (7). An orange 6.0 mM CH₂Cl₂ solution of **1** (95.3 mg, 0.0603 mmol) was bubbled with O₂ for 10 min and stirred for an additional 50 min under an atmosphere of dioxygen. The solvent was removed in vacuo, and the residue was extracted into 1.5 mL of CH₂Cl₂. Vapor diffusion of pentane into the solution yielded orange crystalline clusters of **7**, one of which was used for X-ray diffraction studies. Although the structure of **7** could be determined, bulk samples could not be obtained.

[Fe₂(μ-OH)₂(μ-O₂CAr^{4-FPh})₂(O₂CAr^{4-FPh})₂(OH)₂(2-Ph₂P(O)py)₂] (8). A bright yellow 5.80 mM toluene solution of **3** (190 mg, 0.117 mmol) was bubbled with dry dioxygen for 10 min and stirred for an additional 50 min under an atmosphere of O₂. The solvent was then reduced under vacuum leaving a residue that was extracted into 1.5 mL of CH₂Cl₂. Bright yellow block crystals of **8** (49.3 mg, 25%) suitable for X-ray diffraction studies were isolated by diffusing pentane into the solution. FT-IR (KBr, cm⁻¹): 3572 (m), 3432 (br), 3057 (w), 1735 (w), 1604 (s), 1511 (s), 1455(s), 1407 (m), 1345 (s), 1222 (s), 1159 (s), 1136 (m), 1095 (w), 1009 (w), 839 (s), 808 (s), 791 (s), 771 (m), 736 (w), 698 (s), 555 (s), 536 (s), 460 (w), 414 (w). Anal. Calcd for C₉₃H₆₂NFe₂O₁₂F₈P: C, 66.48; H, 3.72; N, 0.83; P, 1.84. Found: C, 66.23; H, 3.69; N, 0.76; P, 1.58.

Physical Measurements. FT-IR spectra were recorded on a Thermo Nicolet Avatar 360 spectrometer with OMNIC software. ¹H NMR data and ³¹P NMR spectra were recorded on Varian 300 and Varian 500 spectrometers, respectively; both spectrometers are housed in the Massachusetts Institute of Technology Department of Chemistry Instrument Facility (MIT DCIF). Chemical shifts were referenced to the residual solvent peaks for proton experiments and

to an external standard, H₃PO₄, for ³¹P experiments. All spectra were recorded at ambient probe temperature, 293 K.

X-ray Crystallographic Studies. Intensity data were collected on a Bruker (formerly Siemens) APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), controlled by a Pentium-based PC running the SMART software package.³² Single crystals were mounted on the tips of glass fibers, coated with paratone-N oil, and cooled to -100 °C under a stream of N₂ maintained by a KRYO-FLEX low-temperature apparatus. Data collection and reduction protocols are described elsewhere.³³ The structures were solved by direct methods and refined on F² by using the SHELXTL-97 software³⁴ incorporated in the SHELXTL software package.³⁵ Empirical absorption corrections were applied with SADABS,³⁶ part of the SHELXTL program package, and the structures were checked for higher symmetry using PLATON.³⁷ All non-hydrogen atoms were located, and their positions were refined with anisotropic thermal parameters by least-squares cycles and Fourier syntheses. In general, hydrogen atoms were assigned to idealized positions and given thermal parameters equivalent to either 1.5 (methyl hydrogen atoms) or 1.2 (all other hydrogen atoms) times the thermal parameter of the carbon atom to which they were attached. The structure of **3** has one dichloroethane molecule in the lattice in which one of the chlorine atoms is disordered over two positions and was refined with a 70/30 occupancy. Four carbon atoms in one of the *p*-fluorophenyl rings were disordered over two positions and were refined at 50% occupancy. In the structure of **4**, one of the ⁻O₂CAr^{Tol} ligands was disordered and was modeled over two positions with 50% occupancy. A pentane and 1.5 dichloroethane molecules are present in the unit cell of **4**. The pentane molecule is severely disordered, and each carbon atom was modeled over three positions using identical anisotropic displacement parameters. The half dichloroethane molecule lies on a center of symmetry; the chlorine atom is disordered and was refined with the atoms distributed equally over two positions. Compound **5** has a chlorobenzene molecule in the crystal lattice. The structure of **7** has four CH₂Cl₂ molecules in the lattice. The structure of **8** has three CH₂Cl₂ molecules in the lattice. The structures of **3–8** are shown in Figures 1–3 and S1–S6 (Supporting Information). Data collection and experimental details are summarized in Table S1; those for **1** and **2** were reported previously.²⁸ Selected bond lengths and angles for **1–8** are provided in Tables 1, 2, and S2–S4.

Mössbauer Spectroscopy. Mössbauer spectra were recorded on an MSI spectrometer (WEB Research Co.) with a ⁵⁷Co source in a Rh matrix maintained at room temperature in the MIT DCIF. Solid samples of **6** and **8** were prepared by suspending ~0.024 mmol of the yellow powdered material in Apeizon N grease and coating the mixture on the lid of a nylon sample holder. Data were collected at 4.2 K, and the isomer shift (δ) values are reported with respect to the natural iron foil that was used for velocity calibration at room temperature. The spectra were fit to Lorentzian lines using the WMOSS plot and fit program.³⁸

Oxidation Product Analyses. Oxidation reactions were performed by exposing CH₂Cl₂ solutions of the diiron(II) complex to

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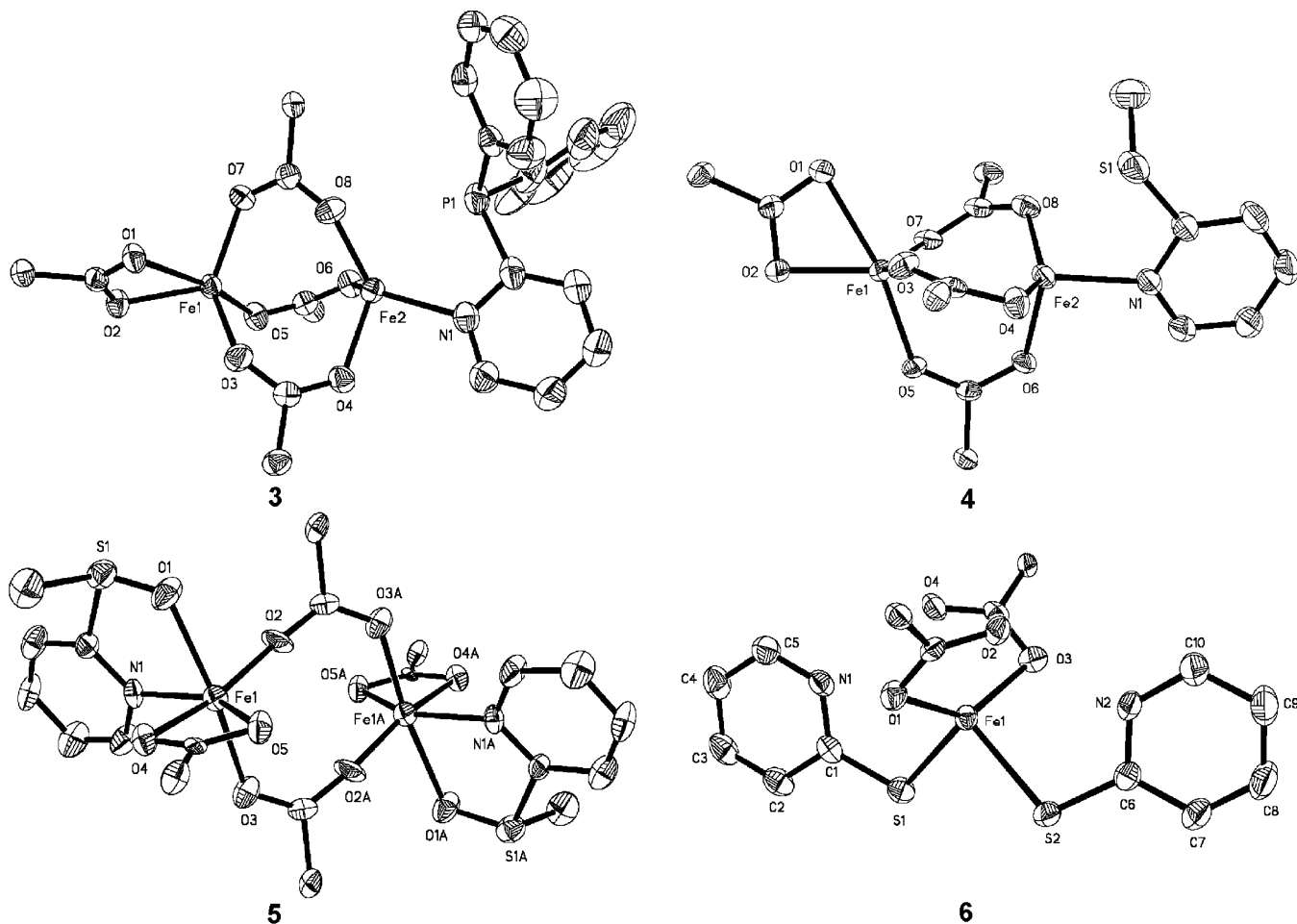


Figure 1. ORTEP diagrams of $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^4\text{-FPh})_3(\text{O}_2\text{CAr}^4\text{-FPh})(2\text{-Ph}_2\text{Ppy})]$ (**3**), $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_3(\text{O}_2\text{CAr}^{\text{Tol}})(2\text{-MeSpy})]$ (**4**), $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_2(\text{O}_2\text{CAr}^{\text{Tol}})_2(2\text{-MeS(O)py})_2]$ (**5**), and $[\text{Fe}(\text{O}_2\text{CAr}^{\text{Tol}})_2(2\text{-HSpy})_2]$ (**6a**) showing 50% probability thermal ellipsoids for all non-hydrogen atoms. The aromatic rings of carboxylate ligands are omitted for clarity.

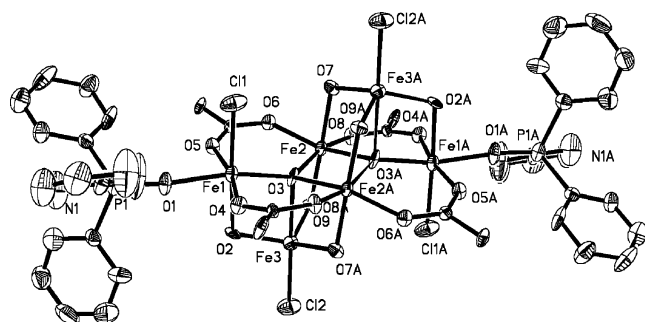


Figure 2. ORTEP drawing of $[\text{Fe}_6(\mu_4\text{-O})_2(\mu\text{-OH})_6(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_4\text{Cl}_4(2\text{-Ph}_2\text{P(O)py})_2]$ (**7**) illustrating 50% probability thermal ellipsoids for all non-hydrogen atoms. The aromatic rings of the $\text{O}_2\text{CAr}^{\text{Tol}}$ ligands are omitted for clarity.

dioxygen at room temperature over a period of time and, in the case of **1** and **3**, also in the presence of added 2-Ph₂Ppy. During workup, Chelex was added to the reaction solutions to remove the iron salts. The resulting slurry was stirred for 2 h, after which the Chelex was removed by filtration. The resin was washed with CH₂Cl₂ twice more, and the filtrates were combined. The solvent was removed in vacuo to give the N-donor species for analysis. The products were identified by NMR spectroscopy and GC-MS by comparing their NMR spectra, retention times, and mass spectral patterns to those of authentic samples. The amount of oxidized ligand obtained was quantitated by ³¹P NMR spectroscopy, using triphenylphosphine oxide as an internal standard for **1** and **3**, and

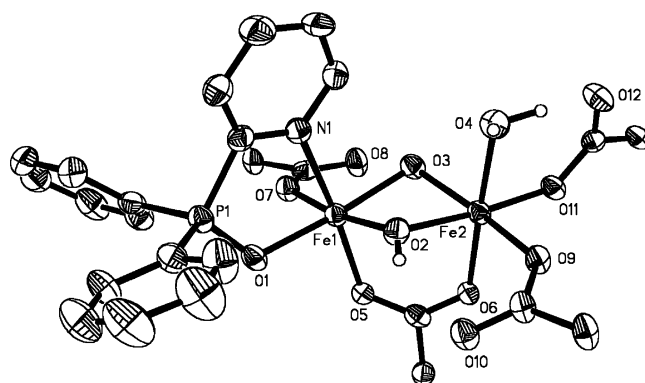
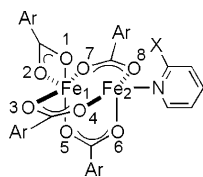


Figure 3. ORTEP drawing of $[\text{Fe}_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CAr}^4\text{-FPh})(\text{O}_2\text{CAr}^4\text{-FPh})_3\text{-(OH)}_2(2\text{-Ph}_2\text{P(O)py})]$ (**8**) illustrating 50% probability thermal ellipsoids for all non-hydrogen atoms. The aromatic rings of the $\text{O}_2\text{CAr}^4\text{-FPh}$ ligands are omitted for clarity.

by GC-MS, using 1,2-dichlorobenzene as an internal standard for **2**, **4**, and **5**. All samples were prepared in an anaerobic glovebox prior to bubbling with dried dioxygen. Control experiments established that, in the absence of the diiron(II) complexes, neither dioxygen saturated CH₂Cl₂ nor the workup procedure induces significant ligand oxidation.

GC-MS Analyses. Analyses were carried out on a Hewlett-Packard HP-5890 gas chromatograph connected to a HP-5971 mass analyzer. An Alltech Econo-cap EC-1 capillary column of dimensions 30 m × 0.53 mm × 1.2 μm was employed with the following

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for [Fe₂(μ-O₂CAr^{Tol})₃(O₂CAr^{Tol})(2-Ph₂Ppy)] (1), [Fe₂(μ-O₂CAr^{Tol})₃(O₂CAr^{Tol})(2-PhSpy)] (2), [Fe₂(μ-O₂CAr^{4-FPh})₃(O₂CAr^{4-FPh})(2-Ph₂Ppy)] (3), and [Fe₂(μ-O₂CAr^{Tol})₃(O₂CAr^{Tol})(2-MeSpy)] (4)^a



	1	2	3	4
Fe1...Fe2	3.3094(6)	3.2712(8)	3.4534(8)	3.2496(7)
Fe2...X	2.8322(7)	3.0897(9)	2.9551(13)	2.9091(10)
Fe1-O1	2.2162(13)	2.2013(16)	2.297(3)	2.256(2)
Fe1-O2	2.0826(13)	2.0869(15)	2.068(3)	2.059(2)
Fe1-O3	2.0512(13)	2.0610(16)	2.000(3)	2.055(2)
Fe1-O5	2.0342(12)	2.0266(15)	2.054(3)	2.026(2)
Fe1-O7	2.0602(12)	2.0484(15)	2.017(3)	2.046(14)
Fe2-N1	2.1314(16)	2.1024(18)	2.127(3)	2.077(3)
Fe2-O4	1.9892(12)	1.9767(16)	2.022(3)	1.977(2)
Fe2-O6	2.0570(12)	2.0155(15)	1.985(2)	2.034(2)
Fe2-O8	1.9981(13)	1.9786(15)	1.998(3)	1.982(12)
O1-Fe1-O2	61.35(5)	61.19(6)	60.07(9)	60.8(15)
O1-Fe1-O3	91.81(5)	88.64(6)	86.96(10)	87.4(16)
O1-Fe1-O5	167.13(5)	109.45(6)	166.37(10)	168.1(15)
O1-Fe1-O7	87.81(5)	92.77(6)	91.98(10)	91.7(16)
O2-Fe1-O3	111.56(5)	109.83(7)	104.65(11)	109.4(17)
O2-Fe1-O5	107.01(5)	169.04(6)	106.30(10)	108.4(16)
O2-Fe1-O7	110.11(6)	114.07(6)	118.47(11)	111.3(18)
O3-Fe1-O5	98.07(5)	89.61(6)	97.32(11)	92.2(16)
O3-Fe1-O7	131.95(5)	130.35(6)	129.17(12)	132.5(17)
O5-Fe1-O7	91.65(5)	95.59(6)	95.25(11)	97.3(16)
O4-Fe2-N1	103.14(6)	106.40(7)	88.53(12)	110(2)
O6-Fe2-N1	91.33(5)	97.36(7)	122.81(12)	95.8(18)
O8-Fe2-N1	111.28(6)	99.52(7)	120.56(12)	100(2)
O4-Fe2-O6	100.35(5)	104.73(6)	103.10(11)	102.1(17)
O4-Fe2-O8	139.10(5)	138.73(7)	122.18(11)	102.4(18)
O6-Fe2-O8	100.29(5)	103.10(6)	99.91(11)	102.4(18)

^a Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated Figures 1, S2, and S3.

program to effect all separations: initial temperature = 100 °C, initial time = 4 min, temperature ramp = 100–210 °C at 20 °C/min, and final time = 4.5 min. Quantitations were made by comparison of the total ion count of 2-PhSpy, 2-PhS(O)py, 2-MeSpy, 2-MeS(O)py, and 2-MeS(O)₂py with that of the 1,2-dichlorobenzene internal standard. Calibration plots for the detector response were prepared for authentic samples of 2-PhSpy, 2-PhS(O)py, 2-MeSpy, 2-MeS(O)py, 2-MeS(O)₂py, and the 1,2-dichlorobenzene standard by using stock solutions of known concentrations.

Oxygenation of 6a. In a typical reaction, compound **6a** was dissolved in CH₂Cl₂ to ~1 mM and loaded into a vessel fitted with a rubber septum. The solution was cooled to -10 °C in an ice/acetone bath. Dioxygen was gently bubbled into the solution, resulting in a color change from pale orange to dark blue that signaled formation of **6b**.

UV-vis Spectroscopy. UV-vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. Low-temperature UV-vis experiments were performed with a custom-made quartz cuvette, 1 cm path length, fused into a vacuum-jacketed dewar. A solution of **6a**, 1.1 mM in CH₂Cl₂ (6 mL), under N₂ was cooled to -10 °C. Dry O₂ was gently purged through the solution for 30 s, and the UV-vis spectra were recorded at various time intervals.

EPR Spectroscopy. EPR spectra were recorded on a Bruker Model 300 ESP X-band spectrometer operating at 9.42 GHz. Temperatures were maintained with an Oxford Instruments liquid

Table 2. Selected Interbond Lengths and Angles for **8^a**

	bond length (Å)		interbond angle (deg)
Fe1...Fe2	2.9725(11)	Fe1-O2-Fe2	98.10(19)
		Fe2-O3-Fe1	97.35(18)
Fe1-N1	2.210(4)	O1-Fe1-N1	80.49(15)
Fe1-O1	2.023(3)	O2-Fe1-N1	84.76(17)
Fe1-O2	1.954(4)	O3-Fe1-N1	92.34(17)
Fe1-O3	1.981(4)	O5-Fe1-N1	172.91(15)
Fe1-O5	2.003(3)	O7-Fe1-N1	92.17(15)
Fe1-O7	1.947(3)	O1-Fe1-O2	97.51(16)
Fe2-O2	1.981(4)	O1-Fe1-O3	172.11(17)
Fe2-O3	1.977(4)	O1-Fe1-O5	93.26(14)
Fe2-O4	2.097(4)	O1-Fe1-O7	89.81(14)
Fe2-O6	2.017(3)	O2-Fe1-O3	78.40(17)
Fe2-O9	1.974(3)	O2-Fe1-O5	92.81(17)
Fe2-O11	1.976(3)	O2-Fe1-O7	171.47(17)
		O3-Fe1-O5	93.68(16)
O2...O10	2.708(6)	O3-Fe1-O7	93.80(16)
O3...O8	2.803(6)	O5-Fe1-O7	91.14(14)
O4...O12	2.537(6)	O2-Fe2-O3	77.85(17)
		O2-Fe2-O4	89.52(19)
		O2-Fe2-O6	91.58(16)
		O2-Fe2-O9	91.96(16)
		O2-Fe2-O11	174.61(17)
		O3-Fe2-O4	88.81(17)
		O3-Fe2-O6	93.02(15)
		O3-Fe2-O9	168.94(16)
		O3-Fe2-O11	97.06(15)
		O4-Fe2-O6	178.02(16)
		O4-Fe2-O9	86.77(17)
		O4-Fe2-O11	88.61(17)
		O6-Fe2-O9	91.55(14)
		O6-Fe2-O11	90.43(14)
		O9-Fe2-O11	92.97(14)

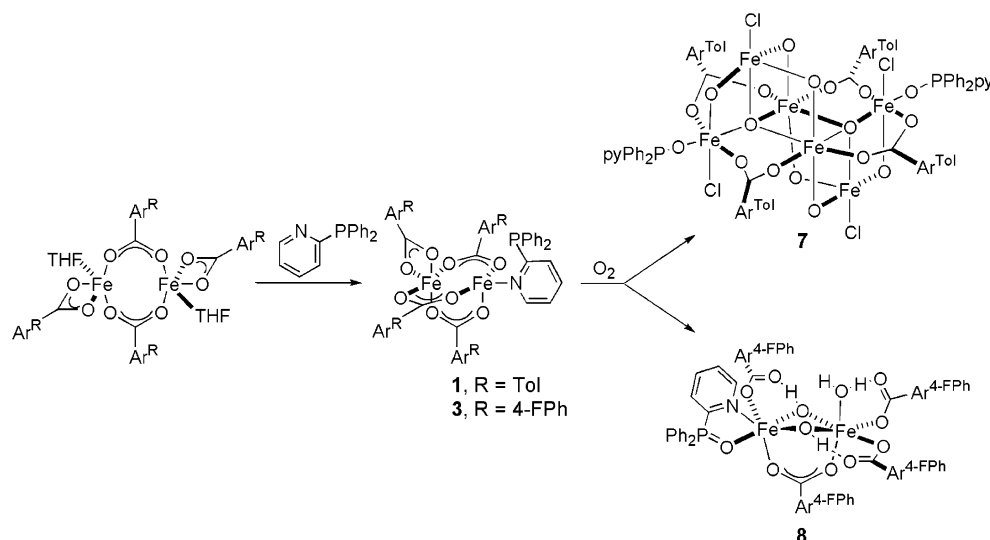
^a Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated Figures 3 and S6.

helium EPR 900 cryostat. X-band EPR samples were prepared by making a 0.513 mM solution of **6a** in CH₂Cl₂. Aliquots of ~300 μL were transferred to the EPR tubes in the drybox; the tubes were septum-sealed. One of the samples was frozen at 77 K. Another was cooled to 4 °C under N₂, treated with O₂ for 45 s, and then frozen at 77 K.

Resonance Raman Spectroscopy. Solutions of **6a** in a J-Young NMR tube were oxygenated with either ¹⁶O₂ or ¹⁸O₂ at -78 °C and subsequently warmed to room temperature for the measurement. The sample was excited at 647.1 nm using a Coherent Innova 90C Kr⁺ ion laser. Plasma lines for the laser were rejected using a holographic band-pass (Kaiser Optical) to obtain a clean background. Approximately 16 mW were focused to a ~100 μm spot. The resulting Raman light was filtered with a holographic notch filter (Kaiser Optical Systems) to attenuate the Rayleigh scattered light and was focused into a 150 μm slit of a single-stage spectrograph (Acton Spectro Pro SP300i). The spectrograph has a 300 mm focal length and is equipped with a 1200 grooves/nm grating giving a linear dispersion of 2.7 nm/mm. The spectral resolution is approximately 5.8 cm⁻¹. Spectra were recorded on a thermoelectrically cooled back-illuminated CCD. The cooling of the CCD to -70 °C significantly reduces the dark current (<0.1 e/p/s).

Prior to each measurement, the Raman system was initially optimized using frozen CH₂Cl₂. The exposure time was adjusted to yield a signal with ~40,000 counts per accumulation, and the total number of exposures taken was adjusted to yield a 5 min gathering. Methylene chloride bands at 1156, 897, 704, and 286 cm⁻¹ were used as a wavelength calibration standard. The sample concentrations were between 2 and 4 mM, and each measurement was made on more than one freshly prepared sample and in triplicate to ensure the authenticity of the results. Data were processed by

Scheme 1



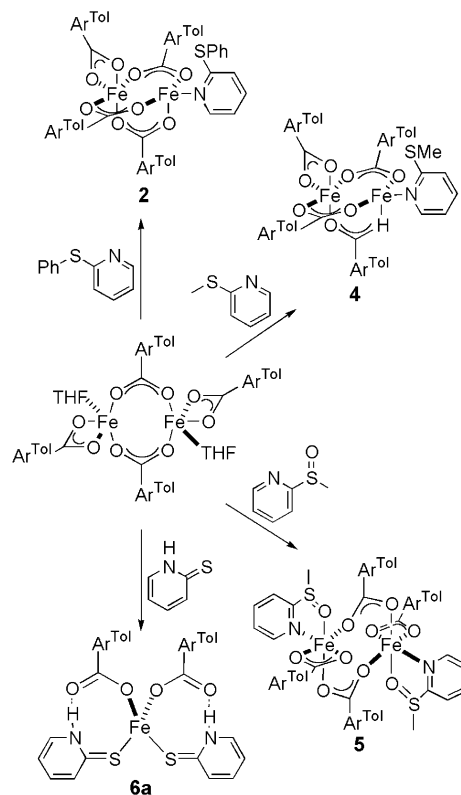
using WinSpec 3.2.1 (Princeton Instruments, Inc.), and the resultant ASCII files were further manipulated using Microsoft Excel.

Results

Synthesis and Structural Characterization of Diiron(II) Complexes with 2-Diphenylphosphinopyridine as the N-donor Ligand: $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_3(\text{O}_2\text{CAr}^{\text{Tol}})(2\text{-Ph}_2\text{Ppy})]$ (**1**) and $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{4\text{-FPh}})_3(\text{O}_2\text{CAr}^{4\text{-FPh}})(2\text{-Ph}_2\text{Ppy})]$ (**3**). Compounds **1** and **3** were prepared by displacement of THF from $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{R}})_2(\text{O}_2\text{CAr}^{\text{R}})_2(\text{THF})_2]$ with 2-Ph₂Ppy, Scheme 1, where R = Tol and 4-FPh, respectively. The structure of **1** was previously reported, but for comparison purposes selected bond lengths and angles are provided in Table 1.²⁸ Figures 1 and S1 show the structure of **3**, and Table 1 lists selected bond lengths and angles. The solid-state structures of **1** and **3** reveal triply carboxylate-bridged diiron(II) centers with Fe···Fe separations of 3.3094(6) and 3.4517(9) Å, respectively. A fourth chelating carboxylate is bound to one of the iron atoms to complete its coordination sphere. On the other metal center, the 2-Ph₂Ppy coordinates through the pyridine nitrogen atom. The Fe···P distance is longer in **3**, 2.9551(13) Å, than in **1**, 2.8322(7) Å. The IR spectrum of **3**, displayed in Figure S7, exhibits features associated with aromatic and carboxylate groups. In addition, the C–F stretches originating from the $\text{-O}_2\text{CAr}^{4\text{-FPh}}$ ligands are visible at 1221 cm^{-1} .³⁹

Synthesis and Structural Characterization of Diiron(II) Complexes with Pendant Sulfur-Containing Substrates $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_3(\text{O}_2\text{CAr}^{\text{Tol}})(2\text{-PhSpy})]$ (**2**), $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_3(\text{O}_2\text{CAr}^{\text{Tol}})(2\text{-MeSpy})]$ (**4**), and $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_2(\text{O}_2\text{CAr}^{\text{Tol}})_2(2\text{-MeS(O)py})_2]$ (**5**). Compounds **2** and **4** differ only in the sulfide substituent. The combination of 2-PhSpy or 2-MeSpy with $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_2(\text{O}_2\text{CAr}^{\text{Tol}})_2(\text{THF})_2]$ led to the isolation of $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_3(\text{O}_2\text{CAr}^{\text{Tol}})(2\text{-PhSpy})]$ (**2**) or $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_3(\text{O}_2\text{CAr}^{\text{Tol}})(2\text{-MeSpy})]$ (**4**), respectively (Scheme 2). The structure of **2** was previously reported, but for comparison purposes selected

Scheme 2



bond lengths and angles are provided in Table 1.²⁸ The structure of **4** is shown in Figures 1 and S2, and selected bond lengths and angles are provided in Table 1. Both **2** and **4** contain triply carboxylate-bridged diiron(II) centers with Fe···Fe separations of 3.2712(8) and 3.2496(7) Å, respectively. The Fe···S distance is longer in **2**, 3.0897(9) Å, compared to that in **4**, 2.9091(10) Å. A fourth bidentate carboxylate ligand completes the metal coordination sphere of the iron atom not bound to a pyridine moiety.

Bright red crystals of **5** were obtained from the reaction of $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_2(\text{O}_2\text{CAr}^{\text{Tol}})_2(\text{THF})_2]$ with 2-MeS(O)py, Scheme 2. Figures 1 and S3 show the structure of **5**, and selected bond lengths and angles are given in Table S2. The

(39) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed.; John Wiley & Sons: New York, 1998.

compound is a doubly carboxylate-bridged diiron(II) species with an Fe \cdots Fe separation of 4.585(3) Å. The coordination sphere of each iron atom is completed by an additional bidentate carboxylate ligand and an N-donor 2-MeS(O)py ligand that is bound through both the N and O atoms, rendering each iron atom 6-coordinate. A five-membered ring is formed involving $\overline{\text{Fe1-N1-C1-S1-O1}}$, with an Fe1-O1 distance of 2.234(5) Å. A comparison of the IR spectra of **4** and **5** (Figure S8) shows the vibrations of two compounds to be nearly identical, with the exception of the S=O stretch at 1008 cm⁻¹ in **5**.³⁹

Isolation of Mononuclear [Fe(O₂CAr^{Tol})₂(2-HSpy)₂] (6a). The combination of one equiv of [Fe₂(μ-O₂CAr^{Tol})₂(O₂CAr^{Tol})₂(THF)₂] with 4 equiv of 2-HSpy, as indicated in Scheme 2, resulted in the formation of the mononuclear iron(II) complex, [Fe(O₂CAr^{Tol})₂(2-HSpy)₂] (**6a**). Its structure is shown in Figures 1 and S4, and selected bond lengths and angles are provided in Table S3. This pseudo-tetrahedral iron(II) complex is coordinated by two monodentate carboxylates and two thioamides bound to the metal center through the sulfur atoms. The largest of the metal-centered bond angles is the O-Fe-O angle of 133.35(9)° and the smallest is the S-Fe-S angle of 92.04(2)°. The other four angles are closer to the ideal tetrahedral value of 109.5°, averaging 105.96(6)°. There is hydrogen bonding between the noncoordinated carboxylate oxygen atoms and the thioamide protons at distances of 2.767(14) Å for O1 \cdots N1 and 2.709(18) Å for O3 \cdots N2. The characteristic S-H stretching absorption in the range of ~2600–2550 cm⁻¹ is absent from the solid-state IR spectrum of **2**, depicted in Figure S9, but the N-H modes are observed at 3196 cm⁻¹.³⁹ This result is consistent with the X-ray structure.

Mössbauer Spectroscopic Properties of 3. The Mössbauer spectrum, measured at 4.2 K, of a solid sample of **3** is pictured in Figure S10. Although the two iron(II) sites differ in coordination environment, there is no evidence for two overlapping signals. The single sharp quadrupole doublet ($\Gamma = 0.37\text{--}0.39$ mm s⁻¹) reveals that the iron centers are indistinguishable by Mössbauer spectroscopy. The quadrupole splitting ($\Delta E_Q = 2.66(2)$ mm s⁻¹) and isomer shift ($\delta = 1.22(2)$ mm s⁻¹) parameters are consistent with those of high-spin iron(II) complexes having oxygen-rich coordination environments, indicating that **3** has a high-spin $S = 2$ ground state.^{23,40}

Reactions of 6a with Dioxygen. When a CH₂Cl₂ or toluene solution of **6a** reacts with dioxygen at -10 °C, a deep blue intermediate (**6b**) develops over a period of 10 min. Absorptions in the UV-vis spectrum, presented in Figure 4, include maxima at 378 ($\epsilon = 3000$ M⁻¹ cm⁻¹), 627 ($\epsilon = 800$ M⁻¹ cm⁻¹), and >1100 nm ($\epsilon \approx 500$ M⁻¹ cm⁻¹). Both the ferrous starting material, **6a**, and the blue intermediate, **6b**, are EPR silent.

Resonance Raman spectroscopy revealed that **6b** contains bound oxygen. Characteristic resonances observed in the

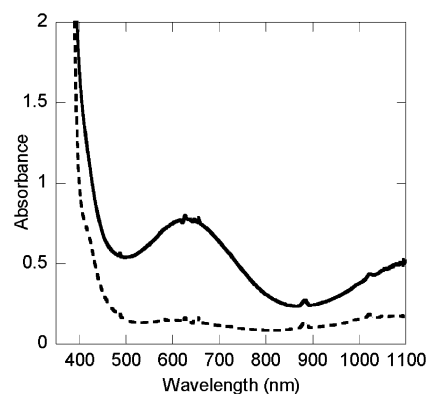


Figure 4. UV-vis spectra of [Fe(O₂CAr^{Tol})₂(2-HSpy)₂] (**6a**) (---) and the intermediate **6b** (—) in CH₂Cl₂ at -10 °C.

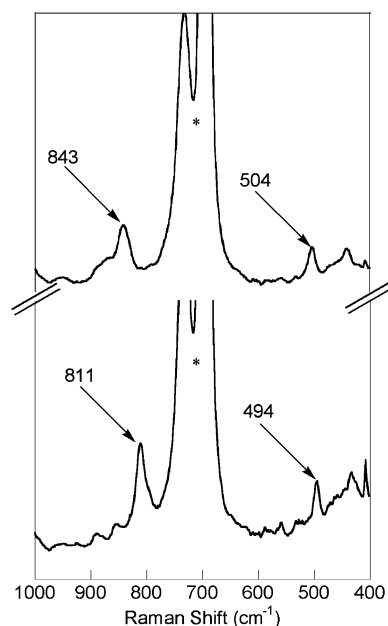


Figure 5. Resonance Raman spectra of a CH₂Cl₂ solution of **6b** derived from the oxygenation of [Fe(O₂CAr^{Tol})₂(2-HSpy)₂] (**6a**) with ¹⁶O₂ (top spectrum) and ¹⁸O₂ (bottom spectrum). The asterisk indicates a solvent band.

Raman spectra of (μ -peroxy)diiron(III) moieties result from O-O (800–900 cm⁻¹) and Fe-O (450–550 cm⁻¹) stretching vibrations.^{23,41,42} Raman spectra were obtained for **6b** in CH₂Cl₂ at room temperature. Upon excitation at 647.1 nm, two Raman active bands appear at 843 and 504 cm⁻¹. These features are absent in the Raman spectra of both **6a** and the decomposition product of **6b**. When the blue intermediate is prepared by reacting **6a** with ¹⁸O-labeled dioxygen (**6b***), the peak positions shift to 811 and 494 cm⁻¹. A comparison of the two spectra is shown in Figure 5.

Tethered Ligand Oxidation in 2, 4, and 5. Oxidation of the substrates appended to the N-donor ligand was investigated by product analysis following the introduction of O₂ into solutions of **2**, **4**, and **5**. A summary of the conditions and the amount of oxidation product recovered is provided in Table 3. A pale yellow CH₂Cl₂ solution of **4** reacts with

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(41) Chavez, F. A.; Ho, R. Y. N.; Pink, M.; Young, V. G., Jr.; Kryatov, S. V.; Rybak-Akimova, E. V.; Andres, H.; Münck, E.; Que, L., Jr.; Tolman, W. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 149–152.
(42) Costas, M.; Cady, C. W.; Kryatov, S. V.; Ray, M.; Ryan, M. J.; Rybak-Akimova, E. V.; Que, L., Jr. *Inorg. Chem.* **2003**, *42*, 7519–7530.

Table 3. Summary of the Conditions and Amount of Oxidation Product Isolated for the Reaction of Compounds **2**, **4**, and **5** with Dioxygen in CH₂Cl₂

compound	[Fe ₂] (mM)	reaction time (h)	oxidized ligand recovered ^a (%)
2	8.6	1.5	29
4	8.2	1.5	58
5	5.1	16	40

^a Based on [Fe₂].

dioxygen at room temperature and immediately turns golden brown. Workup of the mixture and analysis by GC-MS revealed 58% conversion to 2-pyridylmethylsulfoxide (2-MeS(O)py). The unmodified sulfido ligand was quantitatively recovered. The peaks were assigned by comparing the retention times of the M⁺ = 125 and 141 signals with those of authentic samples of 2-methylthiopyridine and 2-methylpyridylsulfoxide. No other products, such as the corresponding pyridyl sulfones, were evident in the GC traces. The analogous oxidation of **2**, analyzed by GC-MS, converts only 29% of the sulfide to the sulfoxide.²⁸

The bright red CH₂Cl₂ solution of **5** becomes dark red-brown upon exposure to dioxygen. Analysis of the products using GC-MS revealed 40% conversion of the 2-MeS(O)py to the sulfone, based on **5**. This assignment was confirmed by comparison of the M⁺ = 157 signal in the GC-MS with an authentic sample of 2-MeS(O)₂py. The remaining material recovered was identified as unaltered pyridylsulfoxide ligand.

Stoichiometric and Catalytic Phosphine Oxidation of the Tethered Phosphine Unit in 1 and 3. Oxidation of the diphenylphosphino group appended to the pyridine ligand was investigated by product analysis following the introduction of dioxygen into solutions of **1** and **3**. Quantitative formation of 2-Ph₂P(O)py occurs within 30 min of the exposure of **1** to dioxygen,²⁸ and the same conversion occurs in the corresponding reaction of **3** in 30 min, with quantitative recovery of the pyridine ligand. Control experiments established that, in the absence of **3**, neither O₂-saturated CH₂Cl₂ nor the workup process induced ligand oxidation over the same time interval (~1 h). ³¹P NMR spectroscopy with Ph₃PO as an internal standard was used to analyze the products of the reaction and monitor the recovery of all species.

Catalytic formation of 2-Ph₂P(O)py ensues when a CH₂Cl₂ solution of **1** is supplied with additional equivalents of 2-Ph₂-Ppy. The results from several experiments show that 4 equiv are converted in an hour and slightly more than 13 equiv are converted over 12 h at a metal complex concentration of 1.5 mM. A 5-fold dilution of the concentration of **1** leads to 17 equiv being oxidized in 17 h. When a phosphine that did not contain a pendant coordinating ligand, such as triphenylphosphine, is added to the reaction mixture, the extent of oxidation is >20-fold less than that from the 2-pyridyl-derivatized phosphine ligand under the same conditions. Catalytic oxidation is not observed to the same degree in MeCN or C₆H₆. In both cases, 2 equiv of 2-Ph₂-Ppy are converted to the phosphine oxide overnight. When a CH₂Cl₂ solution of **3** is provided with more of the pyridine ligand, catalytic phosphine oxidation similarly transpires. A

Table 4. Summary of Conditions and Amount of Oxidation Product Isolated for the Reaction of **1** and **3** with Additional Equivalents of Phosphine and Dioxygen

[Fe ₂] (mM)	compound	2-Ph ₂ Ppy added (equiv)	reaction time (h)	2-Ph ₂ P(O)py recovered ^a (equiv)
2.5	1	8.44	1	3.98
1.4	1	47.0	13	13.4
0.31	1	51.5	17	17.0
3.2	3	8.55	17	2.95

[Fe ₂] (mM)	compound	PPh ₃ added (equiv)	reaction time (h)	(O)PPh ₃ recovered (equiv)
0.42	1	5.62	14	0.70

^a Including 1 equiv of 2-Ph₂Ppy from [Fe₂].

14 h reaction resulted in conversion of 3 out of almost 9 equiv of 2-Ph₂Ppy to the phosphine oxide. This result is comparable to the 13 out of 50 equiv of 2-Ph₂Ppy oxidized under the same conditions by the corresponding ⁻O₂CAr^{Tol} complex, **1**. A summary of the reaction conditions used and the products recovered is provided in Table 4.

Isolation and Structural Characterization of Iron(III) Complexes [Fe₆(μ₄-O)₂(μ-OH)₆(μ-O₂CAr^{Tol})₄Cl₄(2-Ph₂P(O)py)₂] (7**) and [Fe₂(μ-OH)₂(μ-O₂CAr^{4-FPh})(O₂CAr^{4-FPh})₃(OH)₂(2-Ph₂P(O)py)] (**8**).** The hexairon(III) species **7** was isolated as one of the final products from the reaction of **1** with dioxygen (Scheme 2). The structure is best described by the diagrams in Figures 2 and S5, and a list of selected interatomic distances and angles is included in Table S4. The structure of **7** consists two (μ₃-oxo)triiron(III) units that are related by an inversion center and linked through two O²⁻, two OH⁻, and two ⁻O₂CAr^{Tol} bridging groups. Four octahedral and two distorted trigonal bipyramidal iron(III) sites result. A noteworthy feature in the structure of **1** is that two octahedral and two trigonal bipyramidal iron centers are coordinated by chloride ions. Their origin is thought to be a result of solvent oxidation because no comparable material could be obtained when toluene was used as a solvent for this reaction. The two outside iron centers are bound to 2-Ph₂P(O)py, the oxidized N-donor ligand, through the oxygen atom of the phosphine oxide.

Pentane diffusion into the yellow-orange CH₂Cl₂ or toluene solution generated upon oxygenation of **3** produced [Fe₂(μ-OH)₂(μ-O₂CAr^{4-FPh})(O₂CAr^{4-FPh})₃(OH)₂(2-Ph₂P(O)py)] (**8**) (Scheme 1) in 25% yield. The structure of **8** is depicted in Figures 3 and S6, and selected interatomic distances and angles are listed in Table 2. Two distorted octahedral iron(III) atoms are bridged by two hydroxides and one carboxylate ligand. The largest deviations from the ideal 90° interbond angles are 11.60(2)° and 12.15(2)° for Fe1 and Fe2, respectively, and occur at the O-Fe-O angle of the bent four-membered Fe₂(μ-OH)₂ ring. The Fe1-O2-Fe2 unit has Fe1-O2 and Fe2-O2 distances of 1.954(4) and 1.981(4) Å, respectively, and a 98.10(19)° bridging angle. The Fe-O bond lengths in the Fe1-O3-Fe2 unit are slightly longer at 1.981(4) and 1.977(4) Å for Fe1-O3 and Fe2-O3, respectively, but the bridging angle is smaller, 97.35(18)°. The longest Fe-O distances are those to the oxygen atoms of the bridging carboxylate ligand, 2.003(3) and 2.017(3) Å. The Fe...Fe separation of 2.972(1) Å is similar to those

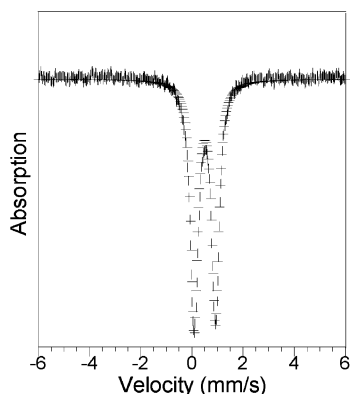


Figure 6. Zero-field Mössbauer spectrum (experimental data (○), calculated fit (—)) recorded at 4.2 K for $[\text{Fe}_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CAr}^{4\text{-FPh}})(\text{O}_2\text{CAr}^{4\text{-FPh}})_3\text{-}(2\text{-Ph}_2\text{P(O)py})(\text{OH}_2)]$ (**8**) in the solid state. See text for derived Mössbauer parameters.

reported for the $\{\text{Fe}_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CR})\}^{3+}$ core in the resting state of MMOH_{ox} ^{43,44} and two other synthetic analogues.^{21,24,45}

In addition to the bridging ligands, one iron atom (Fe1) is coordinated by a monodentate carboxylate group. The other two coordination sites are occupied by O and N atoms from the oxidized N-donor ligand, 2- $\text{Ph}_2\text{P(O)py}$, generating a five-membered Fe1–N1–C1–P1–O1 ring. The other iron center (Fe2) has two monodentate carboxylate ligands and a coordinated water molecule to complete its coordination sphere. Notwithstanding the bridging hydroxide groups, the three monodentate carboxylate ligands provide the shortest Fe–O distances, 1.947(3), 1.974(3), and 1.976(3) Å. The Fe–O bond to the terminally bound water molecule is longer than that to the O atom of 2- $\text{Ph}_2\text{P(O)py}$, 2.099(4) versus 2.023(3) Å. The Fe–N distance of 2.210(4) Å is ~ 0.1 Å longer than that in the diferrous starting material, **3**.

The three terminal carboxylate ligands are involved in hydrogen bonding interactions with the bridging hydroxides, $\text{O}2\cdots\text{O}10$, 2.712(5) Å, and $\text{O}3\cdots\text{O}8$, 2.801(6) Å, and the coordinated water molecule, $\text{O}4\cdots\text{O}12$, 2.537(5) Å. The IR spectrum of **8**, depicted in Figure S7, shows the hydrogen-bonded and non-hydrogen-bonded hydroxide stretches as a broad band centered around 3400 cm^{-1} and a sharper peak at 3572 cm^{-1} , respectively.³⁹

Mössbauer Spectroscopic Properties of 8. The Mössbauer spectrum, recorded at 4.2 K, of a solid sample of **8** is presented in Figure 6. A single sharp quadrupole doublet is observed ($\delta = 0.50(2)\text{ mm s}^{-1}$, $\Delta E_{\text{Q}} = 0.83(2)\text{ mm s}^{-1}$). The isomer shift (δ) falls in the range typical of the high-spin Fe(III) complexes.^{46,47} Although the two iron(III) sites differ, having O_6 and NO_5 donor-atom sets, there is no evidence for two overlapping doublets. The line widths ($\Gamma = 0.31\text{--}0.32\text{ mm s}^{-1}$) are close to natural line widths,

indicating that the two ferric atoms are indistinguishable by Mössbauer spectroscopy.

Bond Valence Sum Analysis of 7 and 8. The bond valence sum (BVS) is an empirical quantity that has been used to determine the oxidation state of metal ions in coordination complexes on the basis of crystallographically determined metal–ligand bond distances.⁴⁸ Bond valences, s_{ij} , between cation i and anion j , are calculated according to eq 1, where r is the observed bond distance and r_o and B are empirically determined parameters. The summation of the bond valences for a particular metal cation yields the oxidation state, V_i . Bond valence sum analysis of both **7** and **8** supports the assignment of the six metal centers in **7** and the two in **8** as iron(III). The calculation of the individual bond valences as well as their summation is available in Table S5.

$$V_i = \sum_j s_{ij} = \sum_j \exp\left(\frac{(r_o - r)}{B}\right) \quad (1)$$

Discussion

In addition to oxidizing methane to methanol, MMOH can accept a variety of oxidizable substrates including methanethiol.³ We therefore investigated 2-mercaptopyridine as an ancillary ligand at the oxygen-rich core of the *m*-terphenyl carboxylate diiron(II) complexes. MMOH also catalyzes the conversion of sulfides to sulfoxides, amines to amine oxides, and olefins to epoxides.^{3,6} The first of these transformations inspired the selection of 2-phenylthiopyridine and 2-methylthiopyridine as N-donor ligands. Although as yet unprecedented in the natural system, the oxidation of dimethyl sulfoxide is thermodynamically more favorable than that of dimethyl sulfide,⁴⁹ so 2-pyridylmethysulfoxide was installed at the $\{\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tot}})_2(\text{O}_2\text{CAR}^{\text{Tot}})_2\}$ core. The oxidation of triphenylphosphine is even more thermodynamically facile, ΔH° being -67 kcal/mol versus -33 kcal/mol for dimethyl sulfide.⁴⁹ Although not a known substrate of the native enzyme, this potentially more reactive species was provided as a 2-diphenylphosphinopyridine ancillary ligand in the carboxylate-rich diiron(II) centers to gain further insight into the chemistry.

Despite the differing substituents on the pyridine and carboxylate ligands, the iron atoms in **1–4** have nearly identical coordination environments. It was initially thought that the steric bulk provided by the diphenylphosphino and phenylthio moieties at the ortho position of the pyridine ring was responsible for only one pyridine ligand being accommodated at the diiron cores in **1–3**. This also proved to be the case in **4** where the heteroatom substituent is a less sterically demanding methyl group. In all four structures, the Fe–O bonds of the three bridging carboxylate ligands are on average 0.05 Å shorter for the iron atom to which the pyridine moiety is coordinated: 2.0191(12) versus 2.0485(13) Å in **1**, 1.9903(15) versus 2.0453(16) Å in **2**,

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2.002(3) versus 2.024(3) Å in **3**, and 1.994(2) versus 2.044(2) Å in **4**. The Fe–O bonds of the terminal carboxylate ligand are the longest and asymmetric at ~2.07 and ~2.25 Å. Such a result reflects the greater electron-releasing character of a pyridine N donor compared with a bidentate carboxylate because the lower-coordinate iron atom would be expected to have the shorter bond lengths, all other things being equal.

When 2-MeS(O)py rather than 2-MeSpy was employed as the N-donor ligand, a more open, doubly carboxylate-bridged structure is adopted for the resulting diiron(II) complex, **5**. Two N donors are now accommodated, compared to only one in the triply bridged complexes, **1–4**. The four Fe–O bond distances range from 1.961(5) to 2.267(5) Å. The Fe···Fe distance of 4.585(3) Å in **5** is >1 Å greater than those observed in the triply bridged structures **1–4** of ~3.3 Å and is quite long, reflecting the *syn,anti* binding mode of the bridging carboxylates.⁵⁰

Instead of the carboxylate-bridged dimetallic unit anticipated upon displacement of the THF molecules in $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tot}})_2(\text{O}_2\text{CAR}^{\text{Tot}})_2(\text{THF})_2]$ by 2-mercaptopyridine, a mononuclear species was isolated. The Cambridge Structural Database reports no other structures of four-coordinate iron containing only sulfur and oxygen ligands; **6a** appears to be the first. The hydrogen bonding between the carboxylate oxygen atoms and the thioamide protons most likely stabilizes this unique mononuclear structure. The iron atom is coordinated by a thioamido ligand, the tautomer of 2-mercaptopyridine (Scheme S1), in which the nitrogen atom is protonated and a carbon–sulfur double bond is present. The C1–S1 and C6–S2 distances of 1.716(3) and 1.717(3) Å are characteristic of C=S double bonds,⁵¹ and the bond lengths of the pyridine ring similarly reflect this assignment.

A single sharp quadrupole doublet occurs in the Mössbauer spectrum of **3**, the quadrupole splitting ($\Delta E_{\text{Q}} = 2.66(2) \text{ mm s}^{-1}$) and isomer shift ($\delta = 1.22(2) \text{ mm s}^{-1}$) values of which are consistent with those of high-spin diiron(II) complexes in oxygen-rich coordination environments.²³ The isomer shift is among the lowest reported for five-coordinate, and slightly higher than those observed for four-coordinate, iron(II) sites (1.0–1.1 mm s^{-1}).⁵² The quadrupole splitting and isomer shift parameters obtained for **3** are slightly lower than those of MMOH_{red} , 3.01 and 1.3 mm s^{-1} , respectively.⁵² This disparity is attributed to complex **3** having fewer nitrogen ligands than the MMOH_{red} active site.

Clues to the identity of the blue intermediate observed upon oxygenation of **6a** are provided by resonance Raman and EPR spectroscopic measurements. The electronic absorption spectrum of **6b** is similar to those of paramagnetic $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ cations formed by other $\{\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tot}})_4\}$ systems, which display intervalence charge-transfer transitions and have a characteristic $g = 10$ signal in their EPR spectra.⁵³

However, both the ferrous starting material, **6a**, and the blue intermediate, **6b**, are EPR silent. The UV–vis spectrum of the latter also resembles those of (μ -peroxo)diiron(III) units in both synthetic analogue and biological systems.^{11,23,54–58} Although **6a** is a mononuclear compound, oxygenation of mononuclear iron(II) can result in diiron(II) complexes, possibly via an $\{\text{Fe}_2(\text{O}_2)\}$ intermediate.⁴⁵ Theoretically, from a simple harmonic oscillator calculation, the downshift upon $^{18}\text{O}_2$ -labeling ($\Delta^{18}\text{O}$) should be -48 cm^{-1} for an O–O stretch and -23 cm^{-1} for the Fe–O stretch. For **6b**, the $\Delta^{18}\text{O}$ values are slightly less (-32 cm^{-1} , -10 cm^{-1}) for the O–O and Fe–O vibrations, respectively, suggesting coupling with other modes in the molecule or possibly an Fe–O–O–X unit.

Oxidation of diphenyl sulfide is slightly more energetically favorable than oxidation of dimethyl sulfide ($\Delta H^\circ = -36$ vs -33 kcal/mol),^{59,60} which is inconsistent with the greater conversion of 2-MeSpy (58%) than that of 2-PhSpy (29%) to the sulfoxide in **4** and **2**, respectively. The higher activity of **4**, despite its carrying the less energetically favorable substrate, may be a result of increased access to the O_2 activated at the diiron center because of the smaller methyl substituent compared to the phenyl group of 2-PhSpy in **2**.

In a study involving $\Delta 9$ -desaturase, which has a carboxylate-bridged diiron site similar to that in MMOH,^{43,61,62} the reaction of 10-thiasterate-ACP with the reconstituted soluble stearoyl-ACP $\Delta 9$ -desaturase complex produced the 10-sulfoxide as the sole product.⁶³ The comparable reaction with 9-thiasearoyl-ACP desaturase, however, gave the 9-sulfoxide as ~5% of the total products. It was concluded that the relative reactivity of the 9- and 10-thia-substituted acyl-ACPs is controlled by the proximity of two positions to the O_2 -activated diiron center in the transition state. The reactivity of compound **4** supports this view. Exposure of **4** to dioxygen leads only to the formation of the sulfoxide. No C–H bond activation of the methyl substituent was observed. Oxidation of an ethyl moiety tethered to pyridine in $[\text{Fe}_2(\mu\text{-O}_2\text{CAR}^{\text{Tot}})_2(\text{O}_2\text{CAR}^{\text{Tot}})_2(2\text{-Etpy})_2]$ produces only α -methyl-2-pyridinemethanol, a result that also may be a consequence of the proximity to the O_2 -activated diiron center.^{27b}

Although the two iron atoms in **5** are coordinatively saturated, the compound readily reacts at room temperature following exposure to dioxygen. The observed ligand oxidation may require carboxylate shifts or partial dissociation of the sulfoxide ligand.²¹ The 40% conversion of the sulfoxide

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to the corresponding sulfone is, to the best of our knowledge, unprecedented in small molecule model compounds but is not surprising from a thermodynamic perspective.^{11,23,64} The ΔH° for the oxidation of dimethyl sulfide to dimethyl sulfoxide is -27 kcal/mol compared to -52 kcal/mol for the oxidation of dimethyl sulfoxide to dimethyl sulfone.⁴⁹ Despite the fact that compound **5** is more sterically hindered than **4**, once dioxygen can access the diiron center and become activated, the ligand oxidation reaction will be more favorable.

The catalytic ligand oxidation exhibited by **1** is difficult to rationalize. Previously, we reported the catalytic oxidation of PPh_3 in the presence of dioxygen by the diiron(II) complex $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_2(\text{Me}_3\text{TACN})_2(\text{MeCN})](\text{OTf})_2$, where $\text{Me}_3\text{-TACN} = 1,4,7\text{-trimethyl-1,4,7-triazacyclononane}$.⁶⁵ This phenomenon was only observed when THF was used as the solvent. Further studies revealed that the corresponding diiron(III) complex, $[\text{Fe}_2(\mu\text{-O})(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_2(\text{Me}_3\text{TACN})_2](\text{OTf})_2$, the only detectable iron-containing species during the reaction, could itself promote the catalysis.⁶⁶ Furthermore, it was determined that phosphine oxidation is coupled to catalytic oxidation of the THF solvent producing a C–C bond cleavage product, which occurs until the phosphine is consumed. For **1**, although autoxidation has not been eliminated, substitution of the added 2- Ph_2Ppy with PPh_3 dramatically decreased the reactivity, >20 -fold, which suggests that the metal center not only initiates the catalysis but that substrate binding and intramolecular oxygenation most likely occur. The reactivity of $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_3(\text{O}_2\text{C-Ar}^{\text{Tol}})(2\text{-Ph}_2\text{Ppy})_2]$ also differs from the previous catalytic system because the reaction also occurs in MeCN and C_6H_6 , albeit with lower conversion, which we attribute to the limited solubility of the starting diiron(II) complex.

A small difference in the remote carboxylate substituents, $\text{O}_2\text{CAr}^{\text{Tol}}$ (**1**) versus $\text{O}_2\text{CAr}^{4\text{-FPh}}$ (**3**), leads to pronounced differences in dioxygen reactivity. Previous work revealed that carboxylate ligands with *p*-tolyl substituents form more reactive diiron(II) centers than the *p*-fluorophenyl analogues for both 2-benzyl- and 2-ethylpyridine derivatives.^{27b} This situation is also apparent for the present 2-diphenylphosphinopyridine complexes because **1** catalytically oxidizes five times the amount of phosphine as is oxidized by **3**. The steric properties of these two terphenyl carboxylate groups are similar so the decrease in catalytic activity between the $\text{O}_2\text{CAr}^{\text{Tol}}$ and $\text{O}_2\text{CAr}^{4\text{-FPh}}$ systems is attributed to electronic factors. The pK_a values of $\text{HO}_2\text{CAr}^{4\text{-FPh}}$ and $\text{HO}_2\text{CAr}^{\text{Tol}}$ are 6.14 and 6.50, respectively,⁶⁷ but there are four such ligands, which amplifies the effect.

The influence of different carboxylates is also manifest in the results of the oxygenation reactions of **1** and **3**, as measured by the final product isolated. Whereas oxidation of **3** leads to the formation of a discrete dinuclear

$\{\text{Fe}_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CR})\}^{3+}$ core, a hexanuclear complex, **7**, is recovered from the reaction of **1** with O_2 . Most notably, the structure of **7** contains coordinated chloride ions. Decomposition of the solvent, CH_2Cl_2 , could generate Cl^- , which may drive the formation of hexanuclear compound **7**. An analogous hexanuclear complex with coordinated chloride ligands was isolated following oxygenation of $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_4(4\text{-CNpy})_2]$, where 4-CNpy is 4-cyanopyridine.⁵² Oxidation of CH_2Cl_2 also occurs in MMOH,³ the product formed being unstable and decomposing to formaldehyde and HCl, so the present results may relate to the enzyme system. Solvent oxidation by **1** would provide the chloride ions observed in the final species isolated, **7**. Our observations of increased C–H activation with more electron releasing ligands at the diiron(II) center suggests that the MMOH active site may be similarly activated.

The synthesis of complexes with a $\{\text{Fe}_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CR})\}^{3+}$ core has been challenging because of the tendency of iron(III) salts to form oligo- or polynuclear clusters. The first such compound to be isolated, $[\text{Fe}_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})(\text{O}_2\text{CAr}^{\text{Tol}})_3(\text{N-Bnen})(\text{N,N-Bn}_2\text{en})]$ (**9**), was generated by oxygenation of $[\text{Fe}_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})_2(\text{O}_2\text{CAr}^{\text{Tol}})_2(\text{N,N-Bn}_2\text{en})_2]$.^{24,25} This approach mimics the chemistry occurring at the enzyme active sites. A second route to the $\{\text{Fe}_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CR})\}^{3+}$ core was discovered during oxygenation of mononuclear $[\text{Fe}(\text{O}_2\text{CAr}^{\text{Tol}})_2(\text{Hdmpz})_2]$, where Hdmpz is dimethylpyrazole, which produced $[\text{Fe}_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CAr}^{\text{Tol}})(\text{O}_2\text{CAr}^{\text{Tol}})(\text{OH}_2)(\text{Hdmpz})_2]$ (**10**).⁴⁵ Representations of **9** and **10** are provided in Chart S1. In the present work, exposure of **3** to dioxygen led to **8**, which has the $\{\text{Fe}_2(\mu\text{-OH})_2(\mu\text{-O}_2\text{CR})\}^{3+}$ unit and is only the third structural mimic of the MMOH_{ox} core structure. There was no evidence for solvent oxidation in this reaction. The $\text{Fe}\cdots\text{Fe}$ and $\text{Fe}-\text{O}_{\text{hydroxide}}$ distances of 2.972(1) and 1.954(4)–1.981(4) Å, respectively, in **8** are similar to those of MMOH_{ox} , in which the $\text{Fe}\cdots\text{Fe}$ distance is 2.99 Å, and the $\text{Fe}-\text{O}_{\text{hydroxide}}$ distances are 1.7–2.2 Å.⁴⁴ In the protein, two histidine and three carboxylate terminal ligands, a bridging carboxylate, and solvent-derived molecules complete the NO_5 donor-atom sets at each metal. A slightly different ligand combination is adopted by **8**, which has an NO_5 set for one iron atom and an O_6 set for the other. One of the O donors is a terminally bound water molecule, exactly like that observed in all structurally characterized forms of MMOH to date.^{43,44} Hydrogen-bonding interactions between axial carboxylate ligands and bridging hydroxide ligands in **8** also are observed in MMOH_{ox} .^{43,44}

The single sharp quadrupole doublet exhibited in the Mössbauer spectrum of **8** differs from the results obtained for MMOH_{ox} from both *Methylococcus capsulatus* (Bath) and *Methylosinus trichosporium* OB3b, both of which have Mössbauer spectra indicating the presence of two slightly inequivalent high-spin iron(III) sites.^{54,68} The isomer shift ($\delta = 0.50(2)$ mm s^{-1}) of **8** falls in the range associated with high-spin Fe(III) complexes^{46,47} and is analogous to those

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Table 5. Mössbauer Parameters for **8**, **9**, **10**, and MMOH_{ox}

	coordinate atoms		δ (mm s ⁻¹)	ΔE_Q (mm s ⁻¹)	ref
	Fe1	Fe2			
8	NO ₅	O ₆	0.50(2)	0.83(2)	<i>a</i>
9	N ₂ O ₄	NO ₅	0.48(2)	0.61(2)	24
10	NO ₅	O ₆	0.45(2)	1.21(2)	45
MMOH _{ox}	NO ₅	NO ₅	0.51(2), 0.50(2) ^b		54
			0.50, 0.51 ^c		68

^a This work. ^b *M. capsulatus* (Bath). ^c *M. trichosporium* OB3b.

reported for MMOH_{ox}. As indicated in Table 5, the quadrupole splitting parameter ($\Delta E_Q = 0.83(2)$ mm s⁻¹) in **8** lies between that of the structurally related compounds **9** and **10**.^{24,45} Their Mössbauer parameters, along with those of **8**, are compared to values of MMOH_{ox} in Table 5. The ΔE_Q values obtained for these three compounds are significantly different, despite similar octahedral coordination geometries at the iron(II) sites. Most reported hydroxo-bridged diiron(III) complexes have quadrupole splitting values of ~ 0.5 mm s⁻¹.⁴⁶ Notably, **8** and **10** have more O-rich coordination environments than **9**, with a H₂O (O-donor) ligand instead of an N-donor ligand on the second iron atom. The {Fe₂-(μ -OH)₂(μ -O₂CR)}³⁺ core in MMOH_{ox}, which also has one terminally bound water molecule,^{43,44} displays the similar ΔE_Q values, 0.79(3) and 1.12(3) mm s⁻¹ and 0.87 and 1.16 mm s⁻¹ for *M. capsulatus* (Bath) and *M. trichosporium* OB3b, respectively.^{54,68} An O-rich metal coordination environment may be the source of the similar ΔE_Q (~ 1 mm s⁻¹) values in **8**, **10**, and the diiron sites of MMOH_{ox}.

Conclusion

Tethered thiol, sulfide, sulfoxide, and phosphine moieties on pyridine ligands serve as substrates for oxidation at O₂-activated carboxylate-bridged diiron(II) centers. Intramolecular oxidation of the heteroatoms in these groups further demonstrates that proximity is important for oxidation. Only the group adjacent to the diiron center is oxidized, since no

methyl group oxidation occurred for the case of 2-methylthiopyridine complex. The reactivity of these compounds is not only affected by the N-donor ligand but also by the remote substituents on the carboxylate ligands. The more electron-releasing carboxylate groups showed increased C–H activation, in agreement with results for related systems having tethered benzyl- and ethylpyridine ligands.^{27b} When the less electron-releasing carboxylate group was used, subsequent solvent oxidation did not occur; instead, the {Fe₂-(μ -OH)₂(μ -O₂CR)}³⁺ core of MMOH_{ox} was recovered having structural and Mössbauer spectroscopic properties analogous to those observed in the enzyme. These observations provide valuable information to guide future work on more advanced MMOH synthetic analogues.

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Supporting Information Available: Table S1 summarizing the X-ray crystallographic information for **3–8**; Tables S2, S3, and S4 providing geometric parameters for **5**, **6**, and **7**; Table S5 describing bond valence sum analyses for **7** and **8**; Chart S1 picturing **9** and **10**; Scheme S1 picturing the tautomer of 2-mercaptopridine; Figures S1–S6 showing ORTEP diagrams of **3–8**; Figures S7–S9 containing FT-IR spectra of **3–6** and **8**; Figure S10 illustrating Mössbauer data and fits for **3**; and X-ray crystallographic files in CIF format for **3–8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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